Superconductivity without Fe or Ni in the phosphides $BaIr_2P_2$ and $BaRh_2P_2$

N. Berry,[1] C. Capan,[1] G. Seyfarth,[1,2] A.D. Bianchi,[2] J. Ziller,[3] and Z. Fisk[1]

[1]*Department of Physics and Astronomy, University of California Irvine, Irvine CA 92697-4575*

[2]*Département de Physique, Université de Montréal, Montréal H3C 3J7 Canada*

[3]*Department of Chemistry, University of California Irvine, Irvine CA 92697-4575*

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Heat capacity, resistivity, and magnetic susceptibility measurements confirm bulk superconductivity in single crystals of $BaIr_2P_2$ (T_c=2.1K) and $BaRh_2P_2$ (T_c = 1.0 K). These compounds form in the $ThCr_2Si_2$ (122) structure so they are isostructural to both the Ni and Fe pnictides but not isoelectronic to either of them. This illustrates the importance of structure for the occurrence of superconductivity in the 122 pnictides. Additionally, a comparison between these and other ternary phosphide superconductors suggests that the lack of interlayer $P-P$ bonding favors superconductivity. These stoichiometric and ambient pressure superconductors offer an ideal playground to investigate the role of structure for the mechanism of superconductivity in the absence of magnetism.

Rare earth intermetallics in the $ThCr_2Si_2$(122) structure have been extensively studied due to their many interesting properties, such as superconductivity(SC), heavy fermion behavior, exotic magnetic order, and quantum criticality[1,2]. The recent discovery of superconductivity in iron pnictides, first in LaFeAsO at 26K[3] and soon after in the AFe_2As_2(A=Alkali metal) family[4], has ignited a new interest in non Cu based high T_c SC. The ternary compounds AFe_2As_2 form in the tetragonal 122 structure and contain the same building blocks of FeAs planes as LaFeAsO, which forms in the tetragonal ZrCuSiAs(1111) structure[4,5]. Band structure calculations show a Fermi surface almost exclusively formed by Fe d-bands[6]. Fe pnictides are also very tunable with pressure or chemical substitution, and critical temperatures(T_c) have reached as high as $55K$ in SmFeAs(O,F)[7] and $38K$ in $(Ba,K)Fe_2As_2$[4]. In both families of compounds, SC is seen to emerge from the suppression of a commensurate antiferromagnetic order with pressure or doping[8,9,10]. Moreover, the long range magnetic order is preceded by (concomitant to) a structural transition in the 1111 (122) compounds[6]. So far, much research has been focused on the magnetic transition metal elements Fe and Ni with As in place of Si in the $ThCr_2Si_2$ structure. The mechanism for SC[11,12] is still a matter of intensive debate and investigation in these compounds.

The As atom can be replaced by the isoelectronic element P forming ternary phosphides in the same 122 structure, as first investigated by Jeitschko et al[13,14]. While SC has not been reported in stoichiometric Fe based ternary phosphides at ambient pressure, it has been observed in $LaRu_2P_2$[14], $BaNi_2P_2$[15], and $SrNi_2P_2$[16] with T_c's $\lesssim$ 4K. Most ternary phosphides grown with Co exhibit local moment magnetic order unlike their Fe or Ni counterparts[17]. Isostructural transitions (tetragonal to collapsed tetragonal) have also been reported in the ternary phosphides under pressure[18,19]. Unlike their As counterparts, these compounds do not show a concomitant magnetic transition[16], except $EuCo_2P_2$ with its Eu moment ordering[20].

This paper reports on single crystal SC in the Co column for the 122 phosphides, namely in $BaIr_2P_2$ and

TABLE I: Structural Parameters and Physical Properties

	a(Å)	c(Å)	d_{P-P}(Å)	T_c(K)	$\gamma(mJ/molK^2)$
$BaIr_2P_2$	3.9469(8)	12.559(5)	3.688(2)	2.1±0.04	9.3±0.6
$BaRh_2P_2$	3.9308(3)	12.574(2)	3.725(1)	1.0±0.04	9.2±0.3
$CaRh_2P_2$	4.0179(3)	9.655(1)	2.241(1)	–	10.7±0.2

$BaRh_2P_2$. This finding emphasizes the importance of the 122 structure for the stability of SC, since it occurs in the Fe, Co, and Ni columns of the periodic table. Rh and Ir are non-magnetic elements in the Co column, between the Fe and Ni columns. This provides the opportunity to investigate SC without infringing upon local magnetic moments, known to be detrimental to conventional SC. Further we show from structural analysis that the interlayer P-P bonding might be a relevant parameter for the occurrence of SC in the 122 phosphides.

Single crystals were grown via the standard metal flux technique[21]. The single crystals of $BaRh_2P_2$ and $CaRh_2P_2$ were grown in Pb flux with a ratio of 1.3:2:2:40. For $BaIr_2P_2$, Cu was added to the Pb flux, to increase solubility, with molar ratios of 1.3:2:2:40:5(Ba:Ir:P:Pb:Cu). The mixtures were placed inside an alumina crucible and then sealed in quartz ampoules with inert atmospheres. All three batches were heated at $1150°C$ for $168h$ and slowly cooled $(4°C/h)$ to $450°C$, at which point the excess flux was decanted. The samples were etched in HCl to remove any excess flux. We have also obtained $BaIr_2P_2$ in polycrystalline form from solid state reaction by mixing stoichiometric amounts of each element and heating it at $900°C$ for $100h$ and then quenched to 300K.

The reaction results are first identified by powder X-ray diffraction. Fig. 1 shows the intensity vs scattering angle Θ for $BaRh_2P_2$ single crystals and for polycrystalline $BaIr_2P_2$ powder. The polycrystalline powder has a composition of 85% $BaIr_2P_2$, 10% $Ba_3(PO_4)_2$ and only a few percent of Ir_2P and IrP_2 binaries. Additional peaks in the $BaRh_2P_2$ spectra are from the Pb flux. Single crystals of both $BaRh_2P_2$ and $BaIr_2P_2$ are also characterized by a rotating crystal X-ray diffractometer. The Rietveld
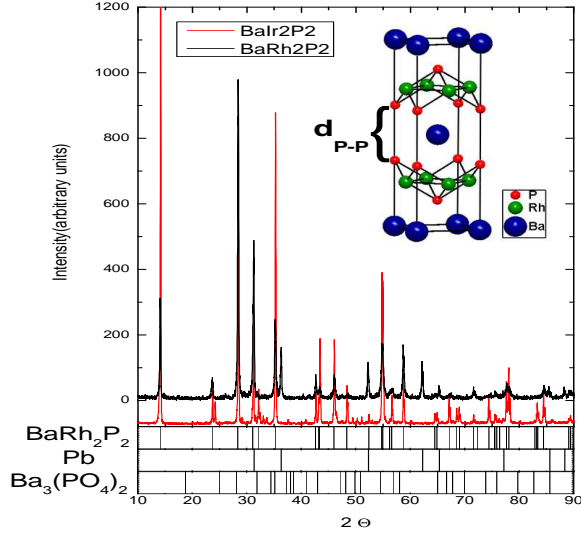
FIG. 1: (Color online)Intensity vs Scattering Angle Θ obtained in powder X-ray diffraction for $BaRh_2P_2$(single crystals) and $BaIr_2P_2$(polycrystals). The vertical lines correspond to the reference pattern of $BaRh_2P_2$, Pb, and $Ba_3(PO_4)_2$[22]. The inset represents the tetragonal unit cell of $BaRh_2P_2$.
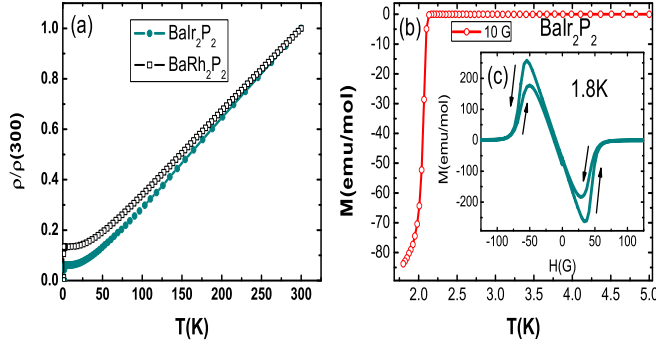

FIG. 2: (Color online) (a) Resistivity(normalized) vs Temperature in the range $0.5-300K$ in single crystals of $BaIr_2P_2$ and $BaRh_2P_2$. (b) Magnetization vs Temperature in polycrystalline $BaIr_2P_2$ showing a diamagnetic jump at $T_c = 2.1K$, in a field of $10G$. (c) Magnetization vs Magnetic Field(H) at $T = 1.8K$ for the same sample.

refinement results are shown in table I and agree with previous reports[23,24]. Moreover, the correct composition and stoichiometry have been confirmed for all single crystals with Energy Dispersive X-ray Analysis. Magnetic properties are measured using a commercial SQUID vibrating sample magnetometer. Heat capacity (C) has been measured using a quasiadiabatic heat pulse technique in a PPMS. The resistivity is measured on a LR700 AC resistance bridge using Pt wires attached with silver paint. The single crystals of $BaIr_2P_2$ were too small for reliable heat capacity and magnetization measurements, so these were carried out on polycrystalline pellets.

The temperature (T) dependence of resistivity (ρ) in single crystals of $BaIr_2P_2$ and $BaRh_2P_2$ is shown in

fig. 2a from $300K$ down to $0.5K$. The high quality of crystals is evidenced by the large residual resistivity ratios($RRR = \rho(300K)/\rho(3K) = 16.5$ in $BaIr_2P_2$ and 7.5 in $BaRh_2P_2$)as well as by the low values of the residual resistivities (8.7 and $1.2\mu\Omega cm$ in Ir and Rh samples). In both systems, $\rho(T)$ exhibits a $T-$linear dependence above $100K$ without any sign of saturation up to $300K$. There is no evidence for structural or magnetic transitions in ρ up to $300K$. At low temperatures, a sharp drop to $\rho = 0$ indicates the onset of SC at $T_c = 2.1K$ in $BaIr_2P_2$ and $1K$ in $BaRh_2P_2$.

The temperature and magnetic field dependence of magnetization (M) are shown in fig. 2b,c for polycrystalline $BaIr_2P_2$. The diamagnetic jump in M(T) corresponds to the same T_c as determined from $\rho(T)$. The magnetization loop M(H) at $1.8K$ shows hysteresis and rather broad extrema. The average of their field positions (necessary due to trapped flux in the magnet) yields 45 Oe as an upper bound for the lower critical field H_{c1} (we adopt the type-II SC scheme since the critical field determined by $\rho(T, H)$ and $C(T, H)$ is significantly higher, see below). The slope of M(H) below H_{c1} is used to estimate that 100% of the volume is superconducting.

The bulk nature of SC is also confirmed with a sharp anomaly in $C(T)$, observed in both compounds (fig. 3a,b). The good agreement between the thermodynamic and resistive T_c and the sharpness of the transition even for the polycrystalline sample imply that T_c does not show any distribution. At zero field, the ratio $\frac{\Delta C}{\gamma T_c}$ equals 1.41 and 1.17 for $BaIr_2P_2$ and $BaRh_2P_2$, consistent with BCS theory. The values of the electronic specific heat coefficient γ are obtained from a linear fit to $\frac{C}{T}$ vs T^2 in the range 0.4-2.4K($BaIr_2P_2$) and 0.5-1.0K($BaRh_2P_2$)(see table I). The γ and T_c shown here are consistent with those reported on polycrystals[25].

The suppression of T_c with magnetic field is seen in $\frac{C}{T}(T)$ (fig. 3a,b) and $\rho(T)$ (fig. 3c,d). In both compounds, the superconducting transition in $\rho(T)$ remains rather sharp, even under magnetic fields as high as $200Oe \approx \frac{H_{c2}}{2}$. This suggests a rather strongly pinned vortex lattice. The specific heat anomaly also remains sharp for the $BaRh_2P_2$ single crystals up to $150Oe$ (see fig. 3b), but broadens with field for the polycrystalline $BaIr_2P_2$ (see fig. 3a). The possible anisotropy of the upper critical field has not been investigated and might be responsible for this broadening. The corresponding $H-T$ phase diagram is shown in fig. 4. There is a good agreement between the values obtained from resistivity and specific heat for both compounds. The use of the approximation $H_{c2}(0) \simeq -0.7T_c\frac{\partial H_{c2}}{\partial T}|_{T_c}$ yields $H_{c2}(0) = 410Oe$ and $370Oe$ in $BaIr_2P_2$ and $BaRh_2P_2$. These values of $H_{c2}(0)$ are comparable to $SrNi_2P_2(390Oe)$[16] and $BaNi_2P_2(550Oe)$[15], but smaller than those cited in Hirai et al[25]. The broadness of the transitions in polycrystals[25] may be the source of the discrepancies. From our values of $H_{c2}(0)$ we estimate the coherence lengths to be 80nm and 95nm for $BaIr_2P_2$ and $BaRh_2P_2$ respectively.

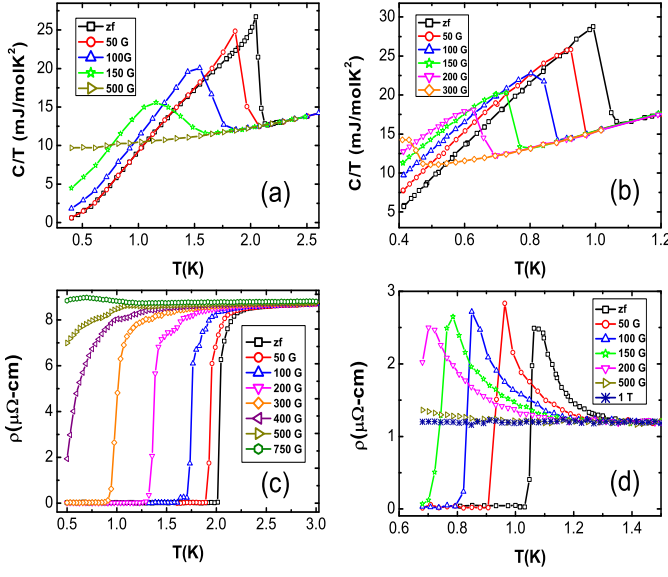Fig. 3d shows a pronounced upturn in $\rho(T)$ preced-

FIG. 3: (Color online) Total $\frac{C}{T}(T)$ at the indicated magnetic fields in polycrystalline $BaIr_2P_2$(a) and single crystals of $BaRh_2P_2$(b). Resistivity vs Temperature at the indicated magnetic fields in single crystals of $BaIr_2P_2$(c) and $BaRh_2P_2$(d).
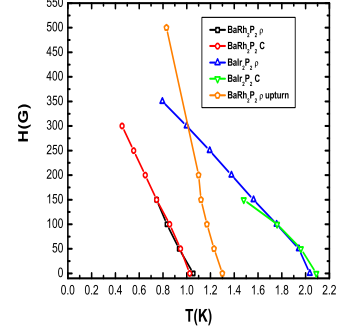

FIG. 4: (Color online) Upper critical field (H_{c2}) vs Temperature in $BaIr_2P_2$ and in $BaRh_2P_2$, as determined from resistivity and specific heat data. Also shown is the onset of the resistivity upturn in $BaRh_2P_2$.

ing the onset of the superconducting jump in $BaRh_2P_2$. The resistivity rises about 100% in the temperature interval 1.35-1K at zero field. The onset of the upturn is suppressed with magnetic field but its amplitude is unaffected. Moreover, this suppression does not appear to be correlated with the upper critical field $H_{c2}(T)$, as seen in fig. 4, suggesting separate phenomena. We have verified that the upturn is present in a second crystal of $BaRh_2P_2$ of similar RRR, as well as in a polycrystalline pellet, but found that the amplitude of the upturn is sample-dependent. A smaller upturn is also observed in single crystal $BaIr_2P_2$ above $700Oe$, but it is absent at zero field in this case. Such an upturn is also reported in $SrNi_2P_2$[16] and $LaFePO$[26]. In addition, a sample dependent Curie tail has been frequently observed in the low temperature susceptibility, with an associated Brillouin like behavior in M vs H for single crystals of both compounds (not shown). The sample-to-sample variation of this magnetic behavior is suggestive of an extrinsic origin, although the corresponding concentration of spin 1/2 is far in excess of the level of magnetic impurities contained in the starting materials ($\leq 20ppm$). Their origin remains unclear and is beyond the scope of this paper.

We now turn to the relationship between the 122 structure and SC in pnictides. $BaFe_2As_2$ is a prime example of the flexibility of this structure on the route to SC: it has been shown that pressure and doping on all three atomic sites have independently induced SC[4,9,10,27]. However, in the isoelectronic $CaFe_2As_2$ the existence of SC is highly controversial[28,29]. Moreover, in $CaFe_2As_2$, recent theoretical calculations show an intimate connection between the Fe-spin state and the interlayer $As-As$ bonding[30].

Future studies should clarify the effect of the Fe moments on T_c. In addition, $BaRh_2As_2$ exhibits no superconductivity down to 1.8K[31]. Thus, the relationship between the tetragonal structure and SC is not clear at present in the 122 arsenides. The present phosphides allow the investigation of the relationship between SC and structure without the interference of magnetism, since neither Rh nor Ir are intrinsically magnetic.

In the ternary phosphides there is an isostructural transition into a collapsed tetragonal structure[18], similar to $CaFe_2As_2$[28,29], except that it does not appear to be associated with any magnetic order[16]. Previous investigations in $BaRh_2P_2$ did not show any structural transition up to $11GPa$ and down to low temperatures[18](no reports for $BaIr_2P_2$). In the phoshpides, unlike the Arsenides, proximity to a structural transition is not a prerequisite for SC. It is known that this isostructural transition corresponds to the formation or breaking of a bond between the interlayer P atoms[32]. In the absence of $P-P$ bond, the cohesion of the layers is due to the Coulomb attraction through the intermediate A^{2+} cation[33]. The critical distance for bond formation obtained theoretically is about $d_c \sim 2.8\mathring{A}$ between the interlayer P atoms, labeled d_{P-P} in the inset of fig. 1[33]. We found that both $BaRh_2P_2$ and $BaIr_2P_2$ have a d_{P-P} of $\sim 3.7\mathring{A}$ (see table I) indicating the absence of interlayer bonding between the P atoms, which is consistent with structural calculations[32]. In contrast, $CaRh_2P_2$ has a d_{P-P} of only $2.25\mathring{A}$, which is below the critical distance for bond formation. We have also grown single crystals of $CaRh_2P_2$ and found no evidence of SC down to $0.55K$. This suggests that the absence of bonds favors SC.

The absence of $P-P$ bonds is also found in other superconducting phosphides, such as $BaNi_2P_2$ which has $d_{P-P} = 3.71\mathring{A}$[34]. In fact, none of the known ternary phosphides ($BaIr_2P_2$, $BaRh_2P_2$, $BaNi_2P_2$[15], and $LaRu_2P_2$[14]) that exhibit ambient pressure SC in the tetragonal structure are bonded between the interlayer P atoms. Nevertheless, it is interesting that $LaRu_2P_2$,

with the highest T_c of $4.1K$, lies closest $(3.00\mathring{A})$ to the theoretical structural instability, while still being in the non-bonding state[14]. However, $SrNi_2P_2$ shows SC in the collapsed tetragonal phase under pressure where a bond exists between the layers[16]. Since the ambient pressure orthorhombic phase is also superconducting it is hard to assess the importance of the structure for SC in this case. De Haas-van Alphen results of $BaNi_2P_2$ show a 3D Fermi surface dominated by the Ni d-bands, indicating that the effect of interlayer coupling on the electronic dimensionality is small[35]. Our results lay the groundwork for more theoretical investigations in order to clarify the relationship between the interlayer bonding and the mechanism for SC in the non-magnetic 122 phosphides.

In conclusion, we have shown the existence of bulk weak coupling SC in 122 pnictides in the Co column of the periodic table with non-magnetic transition metals Rh and Ir. This emphasizes the importance of the 122 structure and the robustness of SC with respect to changes in the electronic configuration, opening the door for SC in other non Fe based compounds. Also, these findings suggest that the lack of interlayer bonding favors SC. It is important to understand how the structure affects SC in the ternary and quaternary pnictides in the absence of competing magnetic order. Due to the apparent lack of magnetism, $BaIr_2P_2$ and $BaRh_2P_2$ provide convenient systems in which to study the interplay between structure and SC.

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